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THE ADSORPTION OF INCOMMENSURATE MONOLAYERS ON AN HEXAGONAL
SUBSTRATE: LEAD UNDERPOTENTIALLY DEPOSITED ON SILVER (111)

by

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THE ADSORPTION OF INCOMMENSURATE MONOLAYERS ON AN HEXAGONAL SUBSTRATE :
LEAD UNDERPOTENTIALLY DEPOSITED ON SILVER (111)

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ABSTRACT

We discuss the incommensurate adsorption of an ad layer on a crystalline substrate. We show that in the case of Pb adsorbed on Ag (111) the size considerations are not enough to determine the angle of epitaxy: A special form of the adsorbing potential is required. The necessary conditions for this potential is discussed. An explicit form for the Pb/Ag(111) case is given.

1-INTRODUCTION

Considerable progress has been made in recent times in the understanding of adsorbed monolayers on solids. Most of the early work however was made on gases adsorbed physically from vapor phase onto graphite or metals^{1 2}. One of the interesting features discovered in this system was the existence of commensurate-incommensurate transitions of the adsorbate, which were observed by LEED³, and explained in terms of models without rotation first^{4 5}, and later by a theory which allows for a variable epitaxy angle between the adsorbate and substrate lattices^{6 7}. In the McTague-Novaco theory⁶, the interaction potential between the adsorbate and substrate is of a simple harmonic form, and the theory predicts a continuous variation of the epitaxy angle as a function of the atom-atom distance of the adsorbate, in good agreement with the LEED experiments of Shaw, Fain and Chinn⁸ of argon on graphite.

In this work we address the problem of the electrodeposition of substrates in general, and metals in particular, in an electrochemical cell. It is only very recently that direct in situ structural information of active electrodes has become available⁹. Although our analysis is dedicated to the underpotential deposited monolayer of lead on ^{the} (111) surface of silver, it can be easily extended to other similar cases of different geometry.

In an early, ex-situ LEED experiment two phases were detected in this system: a low density, commensurate phase and a high density incommensurate phase¹⁰. In the active electrode, however, only the dense phase is observed¹¹. The epitaxy angle is 4.4° , and is not dependent on the lattice constant of the adsorbate, at least within the small range in which this constant can be changed¹². This is in direct contradiction with the McTague Novaco theory⁸, which not only fails to predict the

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correct epitaxy angle, but also cannot account for the locking of the substrate at this fixed angle. This locking can be explained in terms of an adsorption potential that is not harmonic: the purpose of this investigation is to determine the conditions on the adsorbing potential that will explain the value and stability of the epitaxy angle.

We use a simplified model of surface adsorption, to which we can, eventually, incorporate details of a more realistic model of the electrolyte-metal interface. The model uses the sticky potential of Baxter¹³ to represent the adsorption potential. It was used by Perram and Smith¹⁴ to study adsorption of hard spheres onto a smooth, structureless surface. Charged surfaces with discrete adsorption sites were studied in earlier work^{15, 16}.

The most general form of the sticky potential for a surface is

$$e^{-\beta u_i(\underline{r})} = -1 + \lambda(\underline{R}) \delta(z - \sigma_i/2) \quad (1.1)$$

where $\beta = 1/kT$ is the Boltzmann factor, $\underline{r} = (x, y, z)$ is the distance from the interface, situated at the plane $z=0$; $\underline{R} = (x, y)$ is the position on the interface, and we assume that each molecule i has a hard core diameter σ_i .

The function $\lambda(\underline{R})$ is the stickiness of the surface at \underline{R} on the surface. As discussed in earlier work¹⁵, it also represents the fugacity of the adsorbed species, or equivalently, a measure of the chemisorption potential. The symmetry properties of $\lambda(\underline{R})$ should be the same as those of the true adsorption potential $u(\underline{R}, 0)$.

In this paper we discuss the symmetry properties of $\lambda(\underline{R})$ for and hexagonal close packed adsorbate on an hexagonal close packed substrate. This is the case of Pb on Ag(111).

In section 2 the mathematical problem of the appropriate form of $\lambda(\underline{R})$ for the largest adsorption free energy is stated for the hexagonal lattice. The specific case of the Pb/Ag(111) interface is discussed in section 3. We make some general remarks in the concluding section.

2-MATHEMATICAL PROBLEM: THE HEXAGONAL LATTICE

Consider an hexagonal lattice \underline{S} (substrate) with lattice constant a which, for convenience will also be our unit of length ($a=1$). Consider now a second hexagonal lattice \underline{A} (adsorbate) of lattice constant b . The coordinate system for \underline{A} is (x,y) and that of \underline{S} is (x',y') , and the numbers (m,n) and (r,s) define the positions of the points on the lattices \underline{A} and \underline{S} .

The distance d between the points (x, y) and (x', y') is

$$d = [(x_1 - x_0)^2 + (y_1 - y_0)^2 - (x_1 - x_0)(y_1 - y_0)]^{1/2} \quad (2.1)$$

Assume that the coordinates \underline{A} , (x,y) and \underline{S} , (x',y') have a common origin. The angle between the principal axes of \underline{S} and \underline{A} is θ , which is also the epitaxy angle (see figure 1).

The positions of the points of lattice \underline{A} , (m,n) , in the coordinate system (x',y') is given by the equation

$$\underline{X}' = b \underline{M}(\theta) \underline{X} \quad (2.2)$$

where \underline{X}' and \underline{X} are the vectors

$$\underline{X}' = \begin{pmatrix} x' \\ y' \end{pmatrix} \quad \underline{X} = \begin{pmatrix} m \\ n \end{pmatrix} \quad (2.3)$$

and $\underline{M}(\theta)$ is the matrix

$$\underline{M} = \begin{bmatrix} \frac{3-4 \sin^2 \theta}{3 \cos \theta + \sqrt{3} \sin \theta} & 2/\sqrt{3} \sin \theta \\ -2/\sqrt{3} \sin \theta & 2/\sqrt{3} \sin(2\pi/3 - \theta) \end{bmatrix} \quad (2.4)$$

First we would like to investigate the number of overlaps of the points of lattices \underline{A} and \underline{S} : A given point of \underline{S} will overlap with one of lattice \underline{A} if

$$d(\underline{r}_0, \underline{s}_0) = hb \quad (2.5)$$

where $d(\underline{r}_0, \underline{s}_0)$ as given by (2.1) is the distance from the origin to the point $(\underline{r}_0, \underline{s}_0)$ and h is an entire number. The overlap is achieved by turning \underline{A} by

the (epitaxy) angle θ (see figure 1).

Because of the hexagonal symmetry of the problem we need to consider only the interval

$$-30^\circ < \theta < 30^\circ \quad (2.6)$$

It will suffice, therefore to find the set α of pairs (r_o, s_o) with $r_o > 0$ and

$$\begin{aligned} r_o &\geq 2s_o && \text{if } s_o \geq 0 \\ r_o &> |s_o| && \text{if } s_o < 0 \end{aligned} \quad (2.7)$$

that satisfy (2.5). If the set α is not empty, the element (r_o, s_o) such that

$$d(r_o, s_o) = \text{minimum} \quad (2.8)$$

defines one of the points of the coincidence lattice (see figure 1). For symmetry reasons there will be 6 equivalent coincidence points that satisfy equation (2.8) (see figure 1). The epitaxy angle is then given by

$$\theta = \arccos \left[\frac{2r_o s_o}{2(r_o^2 + s_o^2 - r_o s_o)^{1/2}} \right] \quad (2.9)$$

The lattice constant of the coincidence lattice is hb . In figure 1 we display a coincidence lattice where the lattice constant is $3b$ ($h=3$), and $b = \sqrt{13}/3 = 1.2018$.

We introduce the degree of overlap γ of the lattices \underline{A} and \underline{S} as the ratio of the unit areas of each of these lattices to the area of the coincidence lattice. Therefore $\gamma = h^{-2}$. γ is the proportion of points of the substrate lattice that overlapping points of the adsorbate lattice.

Consider now the effective energy function $\lambda(x', y')$ (1.1), which must satisfy the symmetry requirements of lattice \underline{S} . In the absence of any other interaction, the adsorption free energy of the substrate onto the adsorbate is

$$E = h^{-2} \sum_{m=0}^h \sum_{n=0}^h \lambda(x', y') \quad (2.10)$$

where the prime indicates that the sum is over all the points of \underline{A} of the unit coincidence cell (a total of $(h+1)^2$ points). The energy is normalized to the energy per adsorbate atom by h^{-2} , and (x', y') is given by (2.2).

3-A REAL SYSTEM : UNDERPOTENTIALLY DEPOSITED Pb ON Ag (111)

Recent experiments on the Pb/Ag underpotential deposition ^{11 12} have shown that the adsorbate and substrate are hexagonal, with an epitaxy angle $\theta = 4.4^\circ$. The lead-lead distance on the surface lattice is $3.459 \pm .002 \text{ \AA}$ which is 1.2% shorter than in the bulk (3.501 \AA). The lattice constant of Ag is 2.88 \AA for the bulk crystal. If we assume that there is no distortion of the surface layer, then the ratio for the overlayer is $b(ol) = 1.2010$, in contrast to the 'bulk' ratio $b(bulk) = 1.2152$. In table 1 we give the values of (r_\bullet, s_\bullet) that satisfy (2.5) for values of b such that

$$|b - b(ol)| < .002b(ol) \quad (3.1)$$

The experimental situation is that the value of b is not known accurately because the surface layer of the substrate, Ag in this case, may suffer small distortions.

From (2.5) and (2.9) we find

$$\begin{aligned} \sin \theta &= \sqrt{3} s_\bullet / (2hb) \\ \sin (2\pi/3 - \theta) &= \sqrt{3} r_\bullet / (2hb) \end{aligned} \quad (3.2)$$

so that from (2.2) and (2.4) we get :

$$\begin{aligned} x' &= [(r_\bullet - s_\bullet)m + s_\bullet n] / h \\ y' &= [-s_\bullet m + r_\bullet n] / h \end{aligned} \quad (3.3)$$

For the values of (r_\bullet, s_\bullet) , b and θ of table 1, the coordinates of the nodes of the adsorbate are multiples of $1/h$, so that

$$(hx', hy') \in \underline{\underline{Z^2}} \quad (3.4)$$

where $\underline{\underline{Z^2}}$ is the set of ordered entire numbers. If we now choose for the adsorption potential a function of the form

$$\lambda(x', y') = -\cos 2\pi hx' - \cos 2\pi hy' \quad (3.5)$$

then every point of the adsorbate lattice will be situated at a minimum of

the adsorption potential. Although this ideal situation is probably never realized in nature, the requirement is that the Fourier component of largest amplitude of $\lambda(R)$ for a given configuration must be that given by (3.5).

The proposed structures in table 1 are all compatible, within experimental error with the reported spacings^{11 12} of the ad layer, but the epitaxy vary widely.

For the underpotentially deposited Pb on Ag (111) the adsorption parameter $\lambda(R)$ must have its largest component of the form

$$\lambda(x', y') = -\cos 56\pi x' - \cos 56\pi y' \quad (3.6)$$

From table 1 the parameters should be

$$h=28 \quad b=\sqrt{1129/28}=1.2000\dots \quad \theta=\pm 4.43^\circ$$

The energy for this potential is -2, which is an ideal value.

CONCLUSIONS

The preceding discussion shows that for a given ratio of sizes the epitaxy angle can vary over a large range of possibilities. The fact that in the experiment the epitaxy angle is very reproducible and stable, indicates that there must be a special form of the adsorption potential which is responsible for it. Another possibility would be grain boundary effects: However, this is unlikely to be so, because then there would be a much larger degree of disorder in the adlayer, which is not observed.

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TABLE 1

Values of parameters for the adlayer that satisfy (2.8) and (2.11)

$$b(01)=1.2010$$

| $(r_{\bullet}, s_{\bullet})$ | h | b | γ | θ |
|------------------------------|-----|---------------------------|-----------|------------------|
| (4, 1) | 3 | $\sqrt{13}/3=1.2018$ | 3^{-2} | 13.89° |
| (3, -1) | 3 | $\sqrt{13}/3=1.2018$ | 3^{-2} | -13.89° |
| (6, 0) | 5 | $6/5=1.2000$ | 5^{-2} | 0.00° |
| (18, 9) | 13 | $9\sqrt{13}/13=1.1991$ | 13^{-2} | 30.00° |
| (9, -9) | 13 | $9\sqrt{13}/13=1.1991$ | 13^{-2} | -30.00° |
| (35, 3) | 28 | $\sqrt{1129}/28=1.2000..$ | 28^{-2} | 4.43° |
| (32, -3) | 28 | $\sqrt{1129}/28=1.2000..$ | 28^{-2} | -4.43° |

FIGURE CAPTION

Figure 1 : (•) points of the substrate lattice

(○) points of the adsorbate lattice

(⊙) points of the coincidence lattice

The dotted lines indicate a unit cell of the coincidence lattice

$$b=\sqrt{13}/3 \quad h=3 \quad \theta=-13.89 \quad (r_{\bullet}, s_{\bullet})=(3, -1)$$

